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## **Aged black carbon in marine sediments and sinking particles**

Coppola, Alysha I ; Ziolkowski, Lori A ; Masiello, Caroline A ; Druffel, Ellen R M

**Abstract:** We report measurements of oceanic black carbon (BC) to determine the sources of BC to abyssal marine sediments in the northeast Pacific Ocean. We find that the average  $^{14}\text{C}$  age of BC is older (by  $6200 \pm 2200$   $^{14}\text{C}$  years) than that of the concurrently deposited non-BC sedimentary organic carbon. We investigate sources of aged BC to sediments by measuring a sample of sinking particulate organic carbon (POC) and find that POC may provide the main transport mechanism of BC to sediments. We suggest that aged BC is incorporated into POC from a combination of resuspended sediments and sorption of ancient dissolved organic carbon BC onto POC. Our BC flux estimate represents 8–16% of the global burial flux of organic carbon to abyssal sediments and constitutes a minimum long-term removal estimate of 6–32% of biomass-derived BC using the present day emission flux.

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## RESEARCH LETTER

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## Key Points:

- Multipool black carbon data set of  $\Delta^{14}\text{C}$  values, BC/OC%, and BPCA abundances
- A significant fraction of biomass-derived BC is transported to sediments by particulate organic carbon
- Our BC flux estimate represents ~8–16% of the global OC burial flux to sediments

## Supporting Information:

- Readme
- Figure S1
- Table S1
- Table S2
- Equation S1

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## Aged black carbon in marine sediments and sinking particles

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**Abstract** We report measurements of oceanic black carbon (BC) to determine the sources of BC to abyssal marine sediments in the northeast Pacific Ocean. We find that the average  $^{14}\text{C}$  age of BC is older (by  $6200 \pm 2200$   $^{14}\text{C}$  years) than that of the concurrently deposited non-BC sedimentary organic carbon. We investigate sources of aged BC to sediments by measuring a sample of sinking particulate organic carbon (POC) and find that POC may provide the main transport mechanism of BC to sediments. We suggest that aged BC is incorporated into POC from a combination of resuspended sediments and sorption of ancient dissolved organic carbon BC onto POC. Our BC flux estimate represents ~8–16% of the global burial flux of organic carbon to abyssal sediments and constitutes a minimum long-term removal estimate of 6–32% of biomass-derived BC using the present day emission flux.

## 1. Introduction

Black carbon (BC), formed by incomplete combustion of organic matter, cycles on annual to millennial time scales [Masiello and Druffel, 1998; Middelburg et al., 1999]. Black carbon is defined as a continuum from slightly charred plant material to highly graphitized soot [Goldberg, 1985; Schmidt and Noack, 2000; Masiello, 2004]. Char BC is produced by the incomplete combustion of biomass, coals, and other materials, while soot BC is formed from the condensation of combustion gases. Black carbon has been found in marine dissolved organic carbon (DOC) [Dittmar, 2008; Ziolkowski and Druffel, 2010a], particulate organic carbon (POC) [Lohmann et al., 2009; Zigah et al., 2012; Flores-Cervantes et al., 2010], and sedimentary organic carbon (SOC) [Goldberg, 1985; Masiello and Druffel, 2003; Ohkouchi and Eglinton, 2006].

Black carbon enters the ocean by rivers and atmospheric deposition. Modern biomass-derived BC is mainly transported by surface erosion of soils and rivers, delivered to watersheds, and then to the ocean [Foeroid et al., 2011; Major et al., 2010; Rumpel et al., 2006; Hockaday et al., 2007; Jaffé et al., 2013]. Because of its submicron size, soot BC can travel long distances before it is deposited into the ocean [Lohmann et al., 2009; Posfai and Buseck, 2010; Gustafsson and Gschwend, 1998; Ohkouchi and Eglinton, 2006]. Once BC enters the ocean's DOC pool, its chemical and isotopic composition (as measured in ultrafiltered, high molecular weight DOC) dramatically changes between coastal and open ocean regions, suggesting that there are BC loss processes from the marine DOC pool [Ziolkowski and Druffel, 2010a, 2010b; Ward et al., 2014]. Two proposed loss processes are photochemical oxidation in the sea surface [Stubbins et al., 2012] and transport to sediments via sorption to POC [Flores-Cervantes et al., 2010; Zigah et al., 2012].

Marine sediments contain a significant amount of BC in organic carbon, with BC/OC% values ranging from  $15 \pm 2\%$  to  $21 \pm 6\%$  in abyssal sediments and up to  $50 \pm 40\%$  in coastal sediments [Verardo and Ruddiman, 1996; Masiello and Druffel, 1998, 2003; Gustafsson and Gschwend, 1998; Middelburg et al., 1999; Lohmann et al., 2009]. The variability of sediment BC/OC% values is partly due to differences in methods used to quantify BC and to environmental transformations not accounted for by the analytical method used [Hammes et al., 2007; Currie et al., 2002]. Masiello and Druffel [1998] measured  $15 \pm 2\%$  BC/OC in sediment (0–50 cm) from the northeast Pacific, with  $^{14}\text{C}$  ages of the SOC BC  $2400 \pm 120$  to  $5400 \pm 520$   $^{14}\text{C}$  years older than concurrently deposited non-BC SOC. This suggested that BC is preaged for thousands of years prior to deposition in the sediments.

Here we report that BC is removed from seawater via sorption to marine POC and subsequently transported to sediments. We compare BC concentration,  $^{14}\text{C}$  analyses, and qualitative BC structural information to

provide the first analysis of multiple pools of oceanic BC. We used the benzene polycarboxylic acid (BPCA) method, which partially oxidizes BC to aromatic carboxylic acids [Ziolkowski, 2009; Glaser *et al.*, 1998; Brodowski *et al.*, 2005]. Greater aromaticity of a BC sample results in a greater number of acid functional groups on each remaining BPCA. All BPCAs greater than B3CAs were operationally defined as BC, while B2CAs were not quantified because they may be derived from processes other than incomplete combustion, e.g., lignin and humic materials [Brodowski *et al.*, 2005]. Recent modifications of the BPCA method have improved the analytical range of BC detection in the continuum from char to soot [Ziolkowski *et al.*, 2011]. The resulting relative BPCA abundances provide structural information [Glaser *et al.*, 1998; Dittmar, 2008; Ziolkowski and Druffel, 2010a] that aids in identifying BC sources and transformation processes. Using the BPCA method, combined with  $^{14}\text{C}$  analyses, we find that sinking POC is likely the main delivery mechanism of BC to abyssal sediments in the NE Pacific.

## 2. Methods

Sediments were collected from 4100 m depth at Station M (34°50'N 123°00'W), located on the Pacific abyssal plain. The California current flows southward at Station M and has well-developed spring blooms that last until the summer. The sinking POC sample analyzed here is sediment trap material from several time periods collected at Station M at 3450 m depth (650 m above bottom) from 1994 to 1996 (Table S2 in the supporting information) using a conical, moored sediment trap [Smith and Kaufmann, 1999]. Sediments were stored at  $-20^{\circ}\text{C}$  and later dried at  $40^{\circ}\text{C}$  prior to analysis. Additional details of these samples are described in Hwang *et al.* [2004]. We used sediment from a box core (0–14 cm depth, Event 3109) and from a gravity core (26–28 cm, Event 3142) collected in October 1996 [Masiello and Druffel, 1998]. The mixed layer was in the top 8 cm of the sediment [Bauer *et al.*, 1995].

Marine sediments were pretreated to remove polyvalent cations and metals that interfere with BPCA analysis [Brodowski *et al.*, 2005; Coppola *et al.*, 2013] through high temperature and high-pressure digestion in trifluoroacetic acid. The pretreated sediment solution was passed through prebaked, quartz filters and washed with Milli-Q water. Sediment retained on the quartz filters was dried then placed in a quartz vial for high temperature, high-pressure digestion with concentrated nitric acid [Ziolkowski, 2009]. Filtrates were passed through a cation exchange column to remove heavy metals and then freeze dried. The carboxylic acids on BPCAs were derivatized with (trimethylsilyl) diazomethane according to Ziolkowski [2009]. Radiocarbon values were corrected for the  $^{14}\text{C}$ -free C introduced from this methylation [see Coppola *et al.*, 2013]. The BPCAs were identified by comparison with commercially available BPCAs, and mass fragmentation patterns run on a Finnigan Trace mass spectrometry (MS) and gas chromatography with electrospray ionization mass spectrometry (GC/MS ESI) at the University of California, Irvine [Coppola *et al.*, 2013]. Methylated BPCAs were quantified to measure relative BPCA abundances and isolated for  $^{14}\text{C}$  analysis using a Hewlett Packard 6890 preparative gas chromatography with a flame ionization detector coupled to a fraction collector (preparative capillary gas chromatography (PCGC)). Based on retention times of known standards, the PCGC fraction collector was programed to collect B3CAs (BPCA substituted with three carboxylic acids) through B6CAs (those substituted with six carboxylic acids) into a single trap, including the nitrated BPCAs. The BPCA method requires a conversion factor to convert the mass of BPCA C to an estimate of total BC mass in the original sample. We used the conversion factor  $25.8 \pm 6.8\%$  C determined by Ziolkowski and Druffel [2010b].

For  $^{14}\text{C}$  analysis of bulk samples, dried sediment ( $\sim 50$  mg) and POC ( $\sim 15$  mg) samples were acidified with 3% phosphoric acid in quartz tubes and subsequently dried according to Hwang [2004]. Percent organic carbon (%OC) was determined by the manometric measurement of  $\text{CO}_2$  produced from single-tube combustions. Due to the large sediment sample size (1000 mg) required for BC  $^{14}\text{C}$  analysis, only one SOC sample was measured in duplicate, and no POC samples were measured in duplicate for  $^{14}\text{C}$ . BPCA isolates from the PCGC fraction collector were transferred to quartz tubes, dried, and combusted to  $\text{CO}_2$  at  $850^{\circ}\text{C}$  with CuO and Ag. Graphite was produced according to standard methods [Santos *et al.*, 2007]. Radiocarbon results are reported as  $\Delta^{14}\text{C}$  [Stuiver and Polach, 1977]. Uncertainties of the  $\Delta^{14}\text{C}$  measurements are determined from the  $\Delta^{14}\text{C}$  difference between duplicate values [Coppola *et al.*, 2013]. Process blank assessments were made, and BC reference materials were analyzed to account for extraneous carbon introduced during chemical processing, PCGC collection, and graphitization [Santos *et al.*, 2007; Ziolkowski and Druffel, 2010b; Coppola

**Table 1.** Measurements of BC Isolated From Northeast Pacific Sediments and POC Using the BPCA Method<sup>a</sup>

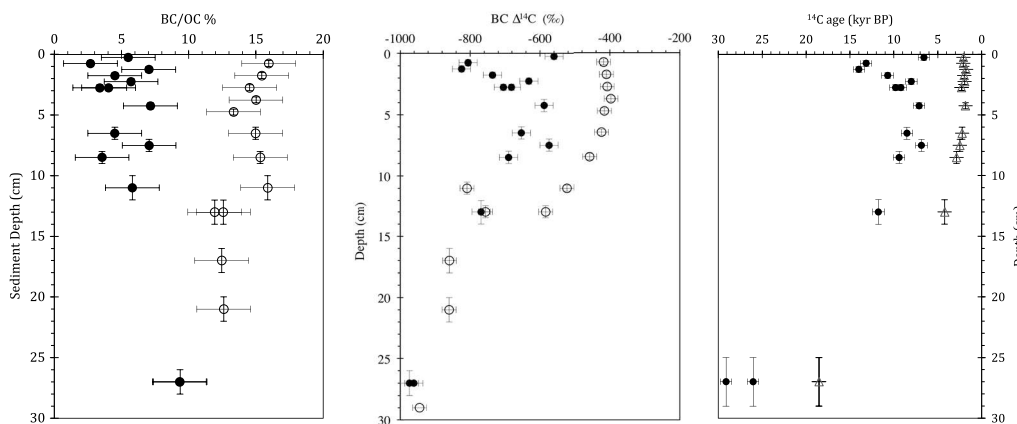
UCID No.	Depth (cm)	OC%	BC/OC%	g BC/kg dry weight	$\Delta^{14}\text{C}_{\text{BC}}$ (‰)	$^{14}\text{C}_{\text{BC}}$ Age ( $^{14}\text{C}$ Years BP)	$\Delta^{14}\text{C}_{\text{bulk}}$ (‰)	$\Delta^{14}\text{C}_{\text{non-BC OC}}$ (‰)
<i>Sedimentary Organic Carbon</i>								
13187	0.25 ± 0.25	1.4 ± 0.4	6 ± 2	0.8 ± 0.4	−530 ± 7	6050 ± 180	−246 ± 4	−229 ± 61
13234	0.75 ± 0.25	1.7 ± 0.2	3 ± 2	0.5 ± 0.1	−740 ± 36	10800 ± 1600	−245 ± 4	−238 ± 90
13241	1.25 ± 0.25	1.5 ± 0.3	7 ± 2	1.1 ± 0.2	−795 ± 18	12700 ± 1030	−242 ± 5	−200 ± 60
13233	1.75 ± 0.25	1.5 ± 0.2	5 ± 2	0.7 ± 0.3	−697 ± 16	9590 ± 620	−242 ± 3	−220 ± 69
13188	2.25 ± 0.25	1.4 ± 0.4	6 ± 2	0.8 ± 0.3	−605 ± 16	7460 ± 470	−238 ± 4	−216 ± 80
<b>13240</b>	2.75 ± 0.25	1.6 ± 0.6	4 ± 2	0.7 ± 0.2	−664 ± 15	8800 ± 520	−263 ± 4	−245 ± 76
<b>13239</b>	2.75 ± 0.25	1.6 ± 0.2	3 ± 2	0.5 ± 0.2	−592 ± 30	7210 ± 870	−263 ± 6	−251 ± 81
13189	4.25 ± 0.25	1.5 ± 0.2	7 ± 2	1.1 ± 0.2	−534 ± 10	6400 ± 270	−231 ± 4	−265 ± 85
13232	6.5 ± 0.5	1.6 ± 0.2	5 ± 2	0.7 ± 0.1	−596 ± 19	7200 ± 540	−260 ± 4	−200 ± 83
13190	7.5 ± 0.5	1.4 ± 0.4	7 ± 3	1.0 ± 0.2	−653 ± 10	6100 ± 240	−286 ± 5	−243 ± 94
13231	8.5 ± 0.5	1.5 ± 0.2	4 ± 2	0.5 ± 0.2	−596 ± 33	7300 ± 790	−312 ± 4	−267 ± 87
13230	13 ± 1	1.5 ± 0.2	6 ± 2	0.9 ± 0.2	−730 ± 18	10500 ± 1300	−428 ± 6	−300 ± 88
<b>12181</b>	27 ± 1	1.0 ± 0.3	9 ± 3	0.9 ± 0.1	−966 ± 21	24300 ± 1700	−904 ± 7	−897 ± 21
<b>12182</b>	27 ± 1	1.0 ± 0.4	9 ± 3	0.9 ± 0.2	−952 ± 15	23600 ± 1400	−904 ± 7	−899 ± 23
<i>Particulate Organic Carbon</i>								
16515	3450m <sup>c</sup>	2.9 ± 0.5	6 ± 2	2.0 ± 0.4	−192 ± 24	2360 ± 260	−12 ± 2	−4 ± 25
<i>Ultrafiltered Dissolved Organic Carbon<sup>b</sup></i>								
11955	1000 m <sup>c</sup>				−918 ± 31	20100 ± 3000	−445 ± 3	−192 ± 24

<sup>a</sup>Bold UCID numbers indicate duplicate measurements.<sup>b</sup>Ziolkowski and Druffel [2010a].<sup>c</sup>Collected from the water column at Station M.

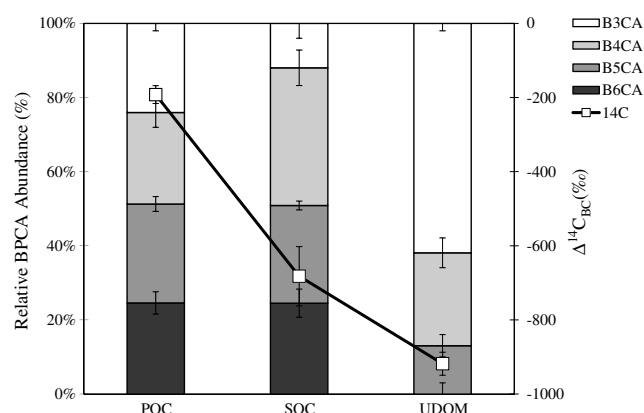
*et al.*, 2013]. BC reference materials, such as wood char and grass char [Hammes *et al.*, 2007], were prepared in varying sizes that bracketed the sample sizes.

### 3. Results

Sediment samples contained  $1.0 \pm 0.3$  to  $1.7 \pm 0.2\%$  OC with an average value of  $1.4 \pm 0.2\%$  OC (Table 1). The BC/OC% in SOC ranged from  $3 \pm 2$  to  $9 \pm 3\%$  (Table 1 and Figure 1a) with an average value of  $6 \pm 2$  BC/OC%. There was no significant trend of BC/OC% with depth (Figure 1a). For the POC sample, OC% was  $2.9 \pm 0.5\%$  and BC/OC% was  $6 \pm 2\%$ . Both POC BC and surface SOC BC have the same BC/OC% values.



**Figure 1.** (a) BC/SOC% with depth in the sediment from Station M. Closed circles represent measurements using the BPCA method (this work). Open circles represent values from Masiello and Druffel [1998] using the  $\text{Cr}_2\text{O}_7$  oxidation method. Sediment depths 0–13 cm were obtained from a box core. A gravity core was used for samples from deeper depths. (b)  $\Delta^{14}\text{C}_{\text{BC}}$  values of sediment samples. Closed circles represent measurements from this work. Open circles represent measurements from Masiello and Druffel [1998] for the same sediment samples. (c) Black carbon  $^{14}\text{C}$  ages (closed circles) plotted with non-BC  $^{14}\text{C}$  ages (open triangles) in sediment using the BPCA method. Non-BC SOC  $\Delta^{14}\text{C}$  values were calculated using a mass balance approach (equation (1) in the supporting information) then converted to  $^{14}\text{C}$  ages in years B.P.



**Figure 2.** Relative BPCA abundances and  $\Delta^{14}\text{C}$  values in SOC BC, POC BC (this work) compared with ultrafiltered DOC BC collected from 1000 m depth [Ziolkowski and Druffel, 2010a] at Station M. Error bars are the standard deviation of measurements. B3CA = hemimellitic, trimellitic, and trimesic acids; B4CA = pyromellitic, prehnitic, and mellophanic acids; B5CA = benzene pentacarboxylic acid; B6CA = mellitic acid and their nitrated compounds.

value of POC was  $-12 \pm 2\text{‰}$ , and the  $\Delta^{14}\text{C}_{\text{BC}}$  value was  $-192 \pm 24\text{‰}$ . Just as for the sediments, the  $\Delta^{14}\text{C}_{\text{BC}}$  value for POC is lower than the  $\Delta^{14}\text{C}_{\text{bulk}}$  value.

The relative abundances of B5CAs and B6CAs in SOC BC (compared to the sum of B3CA + B4CA + B5CA + B6CA) were similar for all depth horizons, averaging  $26 \pm 1\%$  (standard deviation  $n = 12$ ) and  $25 \pm 4\%$  ( $n = 12$ ), respectively (Table S2 in the supporting information). These relative abundances did not vary significantly with depth in the sediment. In contrast, the relative abundances of B4CAs and B3CAs averaged  $36 \pm 4\%$  and  $13 \pm 4\%$ , respectively, but the deepest sediment horizon had lower B3CA and higher B4CA relative abundances than those at shallower depths (Figure S2 in the supporting information). In POC BC, the relative abundances of B3CAs, B4CAs, B5CAs, and B6CAs were similar to those in SOC BC (Figure 2).

#### 4. Discussion

Combustion conditions determine the relative structure of BC. The BPCA method is a powerful tool for constraining the source of BC, because the relative BPCA abundances serve as a fingerprint of the combustion conditions that formed the BC. Hotter combustion conditions, such as during fossil fuel burning, produce a highly condensed BC structure, while cool combustion conditions of biomass burning produce a less condensed BC structure [Schneider *et al.*, 2010]. Additionally, environmental reworking of BC, such as by photochemistry [e.g., Stubbins *et al.*, 2012], can decrease the aromaticity of BC. Therefore, coupling the relative BPCA abundances with compound specific radiocarbon analysis allows us to unravel the sources of BC to marine sediment.

While the main source of OC to POC and SOC at an abyssal ocean site, such as Station M, is water column derived biological material with a modern  $^{14}\text{C}$  content [Hwang *et al.*, 2004], the  $\Delta^{14}\text{C}_{\text{BC}}$  values of SOC and POC are lower than their corresponding  $\Delta^{14}\text{C}_{\text{bulk}}$  values. Therefore, BC in SOC and POC is not of recent biologic origin; instead, it is preaged before it is incorporated into the POC and SOC pools.

A source of old BC to POC and SOC may be sorption of DOC BC onto sinking POC. Ultrafiltered DOC BC from 1000 m depth at Station M is very old ( $20,100 \pm 3000$   $^{14}\text{C}$  years) [Ziolkowski and Druffel, 2010a, 2010b], and a small amount would increase the age of BC in POC substantially. Below we discuss possible sources of preaged BC including sediment resuspension, input via sorption onto sinking POC, and sorption of ancient DOC BC to sinking POC.

First, a source of aged BC to POC and SOC is likely from resuspended sediments that are laterally transported by bottom currents from the continental shelf to the abyssal plain [Hwang *et al.*, 2010]. Using aluminum content and  $\Delta^{14}\text{C}$  values of sinking POC from several open ocean sites, Hwang *et al.* [2010] estimated that  $35 \pm 13\%$  of sinking POC is derived from resuspended sediment and is the primary reason that sinking POC

The  $\Delta^{14}\text{C}$  values of bulk SOC ( $\Delta^{14}\text{C}_{\text{bulk}}$ ) ranged from  $-231 \pm 4\text{‰}$  to  $-904 \pm 7\text{‰}$  (Table 1). In the mixed layer (0–8 cm depth),  $\Delta^{14}\text{C}_{\text{bulk}}$  values ranged from  $-231 \pm 4\text{‰}$  to  $-286 \pm 5\text{‰}$ , and those just below the mixed layer (8.5 and 13 cm) were  $-312 \pm 4$  and  $-428 \pm 6\text{‰}$ , respectively. At 27 cm,  $\Delta^{14}\text{C}_{\text{bulk}}$  values of duplicate samples were both  $-904 \pm 7\text{‰}$ .

The  $\Delta^{14}\text{C}$  values of BC ( $\Delta^{14}\text{C}_{\text{BC}}$ ) for the sediment samples are all lower than SOC  $\Delta^{14}\text{C}_{\text{bulk}}$  values from the corresponding depths (Table 1). Within the mixed layer,  $\Delta^{14}\text{C}_{\text{BC}}$  values ranged from  $-530 \pm 7\text{‰}$  to  $-795 \pm 18\text{‰}$ . Just below the mixed layer,  $\Delta^{14}\text{C}_{\text{BC}}$  values were  $-596 \pm 33\text{‰}$  and  $-730 \pm 18\text{‰}$ , respectively. At 27 cm depth, the average of duplicate analyses was  $-959 \pm 13\text{‰}$  (Figure 1b). The  $\Delta^{14}\text{C}_{\text{bulk}}$



has lower  $\Delta^{14}\text{C}$  values than those in the surface ocean [Hwang *et al.*, 2010]. Bioturbation by macrofauna burrowing and feeding in the mixed layer decreases  $\Delta^{14}\text{C}$  values of SOC at the surface by transporting deeper, older sediments upward from depth making it older than its chronological “age”. Resuspension of the old, surface SOC provides a source of old OC and BC to sinking POC. The similarity of the relative BPCA abundances in POC BC and SOC BC (Figure 2) supports the recycling of resuspended sediment into the sinking POC pool.

A second, though unlikely, source of aged BC to POC and SOC is aerosol soot BC ( $\Delta^{14}\text{C} = -400$  to  $-600\text{‰}$ ) [Gustafsson *et al.*, 2009] that has entered the surface ocean during the past 150 years primarily by atmospheric deposition. In coastal regions, aerosol BC has been shown to play a significant role in transporting BC to the sediments [Flores-Cervantes *et al.*, 2010; Zigah *et al.*, 2012; Lohmann *et al.*, 2009]. Due to the slow sedimentation rate at Station M (1.9 cm/kyr) [Cai *et al.*, 1995], this old BC would constitute a very small amount ( $<4\%$ ) of the BC in the surface sediment, and we do not observe lower  $\Delta^{14}\text{C}_{\text{BC}}$  values in the mixed layer of the sediment relative to those at deeper depths (Figure 1c). Although it could be speculated that deposition has increased at this site, the age offset between BC and non-BC SOC does not appear to change down core, suggesting that the input of preaged BC to SOC was constant before and during the industrial revolution. Therefore, we conclude that this source of  $^{14}\text{C}$ -free BC via aerosols is minimal in these sediments.

The third, and likely the largest source of aged BC to sinking POC and SOC is from DOC. The average  $^{14}\text{C}$  age offset between BC and non-BC SOC of  $6200 \pm 2200$   $^{14}\text{C}$  years (Figure 1c and equation (1) in the supporting information) may represent a residence time for BC in the “holding pool” of DOC before its deposition to the sediments. There are two possible explanations for the different chemical structures of BPCAs in ultrafiltered DOC (no B6CAs) [Ziolkowski and Druffel, 2010a, 2010b] compared to those in POC and SOC (equal amounts of B3CAs, B4CAs, B5CAs, and B6CAs), taking into account the different methodological treatments of these samples (POC and SOC were pretreated with trifluoroacetic acid). We hypothesize that DOC BC may be preferentially sorbed onto sinking POC by (a) aggregation during photolysis or (b) hydrophobic bonding in microgel formation to explain our measurements.

Studies have shown that highly aromatic compounds similar to BC, such as carboxylated multiwalled carbon nanotubes (MWCNTs) and  $\text{C}_{60}$ , lose stability in solution after exposure to UV light, leading to aggregation and deposition in saline solutions [Hou *et al.*, 2010; Hwang *et al.*, 2013; Chen and Jafvert, 2011]. These authors suggested that photochemical transformations can play an important role in the aggregation and deposition of MWCNTs in aquatic systems [Hwang *et al.*, 2013; Saleh *et al.*, 2008]. This mechanism may be important for the transfer of hydrophobic, highly aromatic BC from DOC to POC, leading to an accumulation of smaller, hydrophilic BC structures (yielding B3CA–B5CAs) in oceanic DOC [Ziolkowski and Druffel, 2010a; Masiello and Louchouart, 2013] (Figure 2).

Alternatively, abiotic transfer of BC from DOC to POC may occur synchronously with hydrophobic bonding during marine microgel formation [Verdugo, 2012; Verdugo *et al.*, 2004]. Hydrophobic interactions are low-energy attractions that can cause aggregation and production of POC. It seems likely that hydrophobic BC has a higher aromaticity than hydrophilic BC and would produce a higher B6CA abundance using the BPCA method. Previous work has shown that DOC self-assembled microgel formation facilitates  $\sim 10\%$  of the OC transfer from DOC to POC [Verdugo, 2012; Verdugo *et al.*, 2004]. Whether these processes discriminate between structures of BC is an open question. We hypothesize that aged BC can be incorporated into POC by a combination of resuspended sediments laterally transported from the continental shelf and sorption of aged DOC BC onto POC.

These results can be used to help constrain the flux of BC transported to abyssal sediments via POC, although the flux to coastal sediments is considerably higher [Flores-Cervantes *et al.*, 2010] and limit the scope of our estimate to the open ocean. If we assume that sorption of BC from DOC to POC is the main source of BC to the sediments, the POC flux to the deep ocean is  $2 \text{ mg C m}^{-2} \text{ d}^{-1}$  [Smith and Kaufmann, 1999], and BC/OC% of POC is 6%, we estimate that the average global BC flux is  $0.12 \text{ mg BC m}^{-2} \text{ d}^{-1}$  or  $0.016 \text{ Gt BC yr}^{-1}$ . Because the BC is preaged, this estimate represents the preindustrial era and is at the low end of the range of measured BC flux ranges ( $0.01$  to  $360 \text{ mg m}^{-2} \text{ yr}^{-1}$ ) reported from several studies of the open ocean (see review by Mitra *et al.* [2013]). Our estimate of BC flux represents  $\sim 8$ – $16\%$  of the global burial flux of organic carbon to sediments ( $0.1$  to  $0.2 \text{ Gt C yr}^{-1}$ ) [Hedges and Keil, 1995]. Compared to present day BC biomass emission fluxes ( $0.050$ – $0.270 \text{ Gt BC yr}^{-1}$ ) [Kuhlbusch and Crutzen, 1995], our estimate of POC BC flux to the abyssal ocean represents a removal of 6–32% of biomass-derived BC.

In summary, this multipool data set leads us to conclude that a significant fraction of BC produced from biomass burning could be transported to ocean sediments. However, multiple POC BC and DOC BC measurements are needed to provide a more representative view of BC dynamics in the ocean. Ultrafiltered DOC, from which the only deep ocean BC value was derived [Ziolkowski and Druffel, 2010a], includes only ~25% of the marine DOC pool [Benner, 2002] and does not include the aged low molecular weight fraction [Hansell et al., 2012; Santschi et al., 1995]. Solid phase extraction of DOC [Dittmar et al., 2008] has revealed the presence of B6CAs in North Atlantic Deep Water [Stubbins et al., 2012], which also has a different relative BPCA abundance to that of SOC and POC. Reverse osmosis coupled to electrodialysis (RO/ED) is another method than can be used to isolate >60% of the DOC pool [Vetter et al., 2007; Koprivnjak et al., 2009]. RO/ED has an even greater efficiency for colored DOM absorbance, suggesting it may provide excellent yields of the aromatic compounds contained within colored DOM [Helms et al., 2013]. These data sets would further our understanding of BC cycling in both dissolved and particle phases. Additionally, updated global estimates of sources and sinks of BC are sorely needed to put into context the fate of BC upon entering the ocean.

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